STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION

STUDIES ON THE ULTRA-FINE STRUCTURE OF SOME ILLINOIS COALS

J. S. Machin
Frances Staplin
D. L. Deadmore

STUDIES ON THE ULTRAFINE STRUCTURE
OF SOME ILLINOIS COALS

J. S. Machin, Frances Staplin, and D. L. Deadmore

ABSTRACT

By means of the nitrogen adsorption (BET) method, sur-
face area and pore size measurements have been made on a
number of Illinois high-volatile bituminous coals. These meas-
urements are compared with similar data on a limited number
of other coals of lower and higher ranks. Surface areas for
Illinois samples averaged 3.2 square meters per gram for 3
high-volatile A bituminous coals, 11.8 square meters per gram
for 6 high-volatile B bituminous coals, and 68.4 square meters
per gram for 5 high-volatile C bituminous coals. Irreversible
changes during evacuation caused results for a lignite to be
unreliable; anthracitic coals gave surface area measurements
between those for the high-volatile B and C bituminous coals.

In studies of the banded ingredients of several coals,
vitrains showed the highest specific surfaces, clarain was
lower, and fusain gave the lowest values.

All samples studied showed a predominance of pore
diameters near the value of 40 angstrom units.

The nitrogen adsorption (BET) method is described
briefly.

INTRODUCTION

During a period roughly limited to the years between 1933 and 1955, a num-
ber of papers were published in this country and abroad dealing with the problem
of ultrafine structure of coals. The interest generated by the earliest of these
communications was pointed up by a conference held in England on the Ultrafine
Structure of Coals and Cokes. The proceedings of this conference were published
in book form by the British Coal Utilisation Research Association (1944).

In this country, the problem was attacked by the use of gas adsorption
(BET) methods (Brunauer, Emmett, and Teller, 1938). In England a method based
on measurements of the heat of wetting of pulverized coal in methyl alcohol was

1

favored, partly because it was capable of quickly producing results that were believed to be sufficiently accurate for many purposes. However, it soon became apparent that the two methods gave results which disagreed seriously, sometimes by as much as three hundred or four hundred percent.

Many investigators seriously doubted whether the heat of wetting method could be used properly to measure the surface area of any porous material. These doubts were particularly strong in studying coal with methyl alcohol, which was known to dissolve some material from coal (methyl alcohol takes on a slight brownish color when left in contact with coal) and to cause some swelling of the coal. However, the method has been used often with considerable confidence in applying various liquids to the measurement of the surface areas of nonporous, powdered solids. On the other hand, some people considered that the discrepancies were unexpectedly large.

These doubts led to a reexamination of the gas adsorption method as applied to coal. The most obvious weakness in the method is that the temperature at which the measurements are made is at, or reasonably near, the boiling point of the gas being adsorbed. The most frequently used gases are nitrogen and argon at the boiling point of liquid nitrogen (about 77.5° Kelvin) or of liquid oxygen (about 90° Kelvin).

Coal, unlike other adsorbents containing ultrafine pores, acts as a molecular sieve; that is, small molecules can penetrate coal particles while larger ones cannot. From this fact, one might suspect that at higher temperatures than those mentioned in the preceding paragraph coal might adsorb more molecules because the expansion resulting from warming up would decrease the density and, consequently, increase the pore volume. That this actually happens was shown by Maggs (1952), although the precise mechanisms involved are a matter of conjecture. It might be that constrictions in the pores are opened enough to make available for adsorption surface which is inaccessible at temperatures below 100° Kelvin.

The net result of the controversy was not, as one might hope, a clearcut decision in favor of one method or the other, but a conclusion that the results obtained by the BET method were too low by an unknown amount (probably averaging about 15 percent) and that the methyl alcohol method gave results that were considerably too high. However, interest in the ultrafine structure of coal languished because industry found no application for the data.

At the Illinois State Geological Survey, work on the surface area and pore size distribution of midcontinent coals was carried on intermittently during the decade 1945 to 1955. These coals were not included in studies reported by the U. S. Bureau of Mines, which dealt mainly with eastern coals of rank higher than most coals found in Illinois.

EXPERIMENTAL METHODS

Two types of apparatus were used. The first was similar to that described by Harkins and Jura (1944). The second was a more elaborate and versatile set-up, in many respects similar to one illustrated by Barr and Anhorn (1949, p. 277).

The first step in the determination of the surface area of a powder sample by nitrogen adsorption is carried out by attaching a glass capsule containing a weighed sample of the powder to a vacuum system, pumping the system down to a pressure of the order of 10^{-5} millimeters of mercury, and continuing to pump until

the pressure in the system no longer increases when the system is closed off.

　　　　The second step is to cool the sample to some temperature in the neighborhood of the boiling point of liquid nitrogen by surrounding the sample capsule with liquid nitrogen or liquid air.

　　　　The third step is to admit gaseous nitrogen to the cooled sample capsule at a known pressure in the neighborhood of 0.05 atmospheres and measure the maximum volume of nitrogen that the sample will adsorb at this temperature and pressure. This is repeated at two or three other pressures, the highest of which should be about 0.3 atmosphere. From these volumes and pressures, the surface area may be calculated by means of one of the limiting forms of an equation derived by Brunauer, Emmett, and Teller (1938). This equation in its most general form is

$$V = \frac{V_m C X}{(1 - X)} \left[\frac{1 - (N + 1) X^N + NX^{N+1}}{1 + (C - 1) X - CX^{N+1}} \right] \tag{1}$$

where V is the total volume of gas adsorbed at any given pressure P, V_m is the volume of gas required to cover the surface of the sample with a layer one molecule deep, C is a constant, $X = P/P_0$ where P_0 is the pressure at which the gas being adsorbed would begin to condense to a liquid at the temperature of the measurement and P is the pressure at which the measurement was made, and N is the number of molecular layers that V cubic centimeters of gas would make on the sample if it were evenly distributed.

　　　　The equation in the above form is not convenient for determining the area of the sample. However, as N increases without limit, equation (1) approaches a simplified form:

$$V = \frac{V_m C X}{1 - X} \cdot \frac{1}{1 + (C - 1)X} \tag{2}$$

On replacement of X by its value P/P_0 and an algebraic rearrangement this becomes

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_0} \tag{3}$$

　　　　Equation (3) is in the form of a straight line equation, analogous to $y = b + ax$, where the variables $P/[V(P_0 - P)]$ and P/P_0 correspond to y and x respectively; $1/V_m C$ is the intercept corresponding to the constant b; and $(C - 1)/V_m C$ is the slope corresponding to constant a. V_m and C are constant for any given adsorbent, such as a coal sample, and a given adsorbate, such as nitrogen. V and P are measurable, and P_0 is known when the temperature is known. If a graph is drawn using values of P/P_0 as abscissae and values of $P/[V(P_0 - P)]$ as ordinates, a straight line will result. Its slope, $(C - 1)/V_m C$, and its intercept on the vertical axis, $1/V_m C$, can be measured with satisfactory precision from a large-scale plot. From these it can be calculated that

$$C = \frac{slope}{intercept} + 1$$

and

$$V_m = \frac{1}{slope + intercept}$$

　　　　The determination of V_m is the main object of the experiment. Once it is

known, the total number of nitrogen molecules it contains may be calculated, and multiplication of this number by the area effectively covered by one nitrogen molecule when adsorbed on a surface gives the total area of the surface. The area occupied by one nitrogen molecule is taken as 16.2 Å^2 (Emmett and Brunauer, 1937) for purposes of this report although some workers prefer slightly different values.

It will readily be seen by examination of table 1 that the whole coals of high-volatile C, B, and A bituminous rank from Illinois show a trend in surface area that is strongly downward with increasing rank. If the high-volatile B bituminous rank coals from Indiana are included, the trend, as might be expected, is not changed much.

A few coals from other areas are included, but because the number of samples is so small, the results must be accepted with caution in so far as making generalizations is concerned. It is, however, of interest to note that the surface areas of the anthracite and meta-anthracite samples are much higher than those of the high-volatile A bituminous coals. This may be of interest in connection with theories concerning the final stages in the coalification process, and it should merit more extensive study.

In the case of the lignite sample the very low surface area value is probably not a property of the untreated sample. The lignite sample on evacuation undergoes irreversible changes of uncertain character such that surface area determinations on the resulting product are meaningless. Another interesting fact about this lignite was that the heat of wetting by water of an evacuated sample was about 28.5 calories per gram, which is several times the average for some two dozen other coals on which such measurements were made.

Of the three high-volatile A bituminous coals listed in table 1, the range of surface areas was 1.8 to 4.5 square meters per gram with an average value 3.2.

Six high-volatile B bituminous coals from various Illinois counties ranged from a low of 7.2 to a high of 16.3 square meters per gram with an average of 11.8. For comparison, the area of a sample of Pocahontas (low volatile) coal that happened to be available was found to be 3.2 square meters per gram.

Five Illinois high-volatile C bituminous coals studied ranged from 46.8 to 91.8 square meters per gram. The average was 68.4.

SURFACE AREAS OF BANDED INGREDIENTS

In table 2 surface area measurements on the banded ingredients of samples of Illinois high-volatile A, B, and C bituminous coals are recorded. For all of these samples (except the A rank coal) and various other samples that we have studied, the vitrain always proved to have the highest specific surface. The clarain surface area was less than that of the vitrain and the fusain surface area was least.

In the case of the high-volatile A bituminous coal, the whole coal surface areas were small and, furthermore, it proved difficult to pick out amounts of fusain or clarain of sufficient size to make measurements. For these reasons it was not possible to get more conclusive data on A rank coals of the state.

Adsorption Isotherms on Coal

If adsorption data are plotted according to equation (3) using values of P/P_0 very much greater than 0.35, the points fall below the continuation of the straight line due to the fact that the amounts of gas adsorbed are greater than

TABLE 1 – SURFACE AREAS OF WHOLE COALS

Sample number	Coal rank	Source	Surface area, square meters per gram	Moisture-free volatile matter
C-8652	A[a]	Gallatin Co., Ill.	1.8	40.6
C-7959	A	do.	4.5	37.3
C-5637	A	do.	3.3	37.2
C-6669	B	Franklin Co., Ill.	16.3	———
C-7440	B	do.	9.9	40.0
C-8786	B	Jefferson Co., Ill.	11.6	38.2
C-6668	B	Saline Co., Ill.	7.2	———
C-5593	B	Williamson Co., Ill.	13.2	36.0
C-5598	B	do.	12.7	35.9
C-6452	B	Vigo Co., Indiana	25.8	40.3
C-6448	B	do.	22.4	43.6
C-5651	C	Henry Co., Ill.	66.3	45.4
C-8293	C	do.	58.4	46.8
C-5619	C	Macoupin Co., Ill.	46.8	40.5
C-7052	C	Sangamon Co., Ill.	78.7	42.1
C-9543	C	do.	91.8	———

Miscellaneous Samples

C-5686	Lignite	Velva, N. Dakota	2.8[b]	44.1
C-5707	C[c]	Colorado	4.1[b]	45.0
C-5744	B[c]	do.	31.3	41.1
C-8835	Low-volatile	West Virginia[d]	3.2	16.3
C-5766	Anthracite	Pennsylvania	21.1	3.0
C-8859	Meta-anthracite[e]	Iron River, Michigan	41.8	4.0

a High-volatile bituminous rank in first 16 samples given.

b These two values are probably meaningless because the structure of the samples
   was radically changed by the removal of so much water during evacuation.

c Sub-bituminous

d Pocahontas

e Precambrian

TABLE 2 – SURFACE AREAS OF BANDED INGREDIENTS
(High-volatile bituminous coals)

Sample number	Coal rank	Coal	Source	Surface area, square meters per gram
C-7959	A	Whole coal	Gallatin Co.	4.5
C-7961	A	Vitrain	do.	3.2
C-7440	B	Whole coal	Franklin Co.	9.9
C-7441	B	Vitrain	do.	11.8
C-7442	B	Clarain	do.	6.6
C-7443	B	Fusain	do.	5.9
C-7052	C	Whole coal	Sangamon Co.	78.7
C-7053	C	Vitrain	do.	139
C-7054	C	Clarain	do.	67.6
C-7055	C	Fusain	do.	15.5
C-8293	C	Whole coal	Henry Co.	58.4
C-8294	C	Vitrain	do.	81.7
C-8296	C	Clarain	do.	40.6
C-8295	C	Fusain	do.	11.7

those predicted by equation (3). That is, the equation fits the experimental facts
if the pressure is not greater than about one-third of the saturation pressure of
nitrogen being adsorbed.

In the case of coal it is customary to explain this situation by attributing
the increased adsorption to condensation of the gas to a liquid in small capillaries
present in the coal particles. The classical Kelvin equation

$$D = \frac{-4 \; \sigma V \cos \theta}{RT \; 2.303 \; \log (P/P_0)} \qquad (4)$$

gives the diameter of a capillary in which a gas or vapor will condense to a liquid
and fill the capillary. For highly accurate work, this equation is an oversimplifi-
cation and must be modified. Here D is the pore diameter; σ the surface tension;
V the molal volume of the liquid; θ the angle of contact of the liquid with the capil-
lary wall (for liquid nitrogen on coal the angle θ is assumed equal to zero); R the
gas constant; and T the absolute temperature. Barrett, Joyner, and Halenda (1951)
have worked out a method of computing pore volume and area distributions based on
the Kelvin equation with certain modifications which need not be explained here,
except to say that their modification makes allowance for the fact that the walls
of the pores may hold one or several layers of adsorbed gas molecules before con-
densation begins; thus, the true pore diameter is greater than that calculated from
the Kelvin equation by twice the thickness of the adsorbed layer. It is perhaps un-
necessary to consider this with large pores, but it becomes a very important factor
in the case where many of the pores are only a relatively few molecular diameters
in width.

Because the contact angle appears in the equation, it is evident that we
must consider that we are dealing with a meniscus. The question arises: how
many molecular diameters wide must a pore be before a meniscus can form?
Holmes and Emmett (1947) say: "It is generally agreed that capillary condensation
will not occur at relative pressures lower than that corresponding to four molecular
diameters as calculated by the Kelvin equation." This appears to be an understate-
ment; the diameter usually assumed for the nitrogen molecule (N_2) is about 2 Å,
and the effective area usually assumed to be covered by this molecule on a surface
is about 16.2 $Å^2$. The area of the pore section for a four molecular diameter pore,
therefore, is quite small. This area would be covered by very few molecules.
Whether so few molecules, or even twice that many, could arrange into anything
resembling a meniscus would appear to be questionable.

Nitrogen Isotherms

If adsorption on coal is carried out using nitrogen at the temperature of
liquid nitrogen for a series of values of P/P_0 ranging between zero and one, and
if the total amounts adsorbed are plotted as ordinates and the corresponding P/P_0
values as abscissae, then for low values of P/P_0 the curve rises sharply. As
P/P_0 increases, the curve is concave downward, passing through a point of inflec-
tion at a point averaging somewhere in the neighborhood of $P/P_0 = 0.45$; then it is
concave upward until P/P_0 is about 0.7 or 0.8; from there it is usually, although
not always, concave downward until $P = P_0$. At this point, the sample is saturated
with liquid nitrogen and all open pores are assumed to be full.

For example, if the pressure of nitrogen on the sample is reduced by five
percent, the modified Kelvin equation says that the liquid nitrogen will evaporate
and empty all larger pores down to the specific size corresponding to $P/P_0 = 0.95$.

With proper apparatus we can measure the volume of this nitrogen gas and cal- culate the volume it would occupy as a liquid, which is obviously the volume of the pores that have been emptied. By repeating this process we can arrive at the volume of pores emptied in each interval, and by combining these volumes we can obtain the total volume of all pores larger than any given diameter to which the equation, with reasonable confidence, can be applied. From these data, an estimate of pore size distribution can be made for pores larger than the minimum size for which the equation is valid. For the above reasons, it is agreed generally that it is not safe to apply the method to pores much smaller than 18 or 20 Å diameter. In figure 1, typical nitrogen isotherms for high-volatile bituminous A, B, and C coals of Illinois are shown. The isotherm for coal C-7052 is often referred to as a type IV isotherm (Brunauer, 1945). Those for C-7440 and C-7959 are usually designated as type II. This type differs from type IV; while type IV becomes con- cave downward in the portion near the right hand end of the curve and thus has two points of inflection, type II has only one point of inflection and remains concave upward in the high relative pressure end.

     The isotherm for coal C-7052 is drawn with both the adsorption and desorp- tion branches. That is, the coal was allowed to adsorb the gas at increasing values of P/P_0 from zero up to one; then the process was reversed and the gas allowed to desorb by steps as the pressure was reduced. It will be noted that there is a hysteresis loop between the adsorption and the desorption curves. The area enclosed by this loop decreases as the total pore volume of the sample de- creases. For the Illinois high-volatile C bituminous coal, this area is relatively large. For the Illinois high-volatile A bituminous coal, there is only a relatively small loop.

     From the points on the desorption branch, it is possible to calculate a pore volume distribution curve in terms of the average pore radius between short inter- vals. Figure 2 is such a curve for an Illinois high-volatile C bituminous coal (C-7052). In this figure the abscissae are values of the pore radii in Å units. The ordinates are the values of the total volume ΔV of all pores with radii in the inter- val ΔR divided by the values of ΔR. ΔV is expressed as cubic centimeters per gram of sample. For correcting the pore diameters for layers of adsorbed gas (Barrett, Joyner, and Halenda, 1951), the value 1.94 Å was assumed for the dia- meter of the nitrogen molecule. This curve has a prominent peak in the neighbor- hood of pore radius 20 Å, which indicated that the greater part of the pore volume in this coal is contained in pores around 40 Å diameter. This value kept recurring in such calculations for the coals for which we made these estimates.

     For the banded ingredients, the isotherms in general are similar in charac- ter to those of the whole coal but differ in the areas within the hysteresis loops. That is, if the ingredient has a larger surface area or a smaller surface area than the whole coal, the loop is correspondingly larger or smaller.

Water Isotherms

     A number of isotherms were run on the water adsorption of coals because the moisture content and its variations with relative humidity and other weather factors is of interest in the marketing of coal on specification.

     To obtain data for water isotherms, the technique is necessarily somewhat
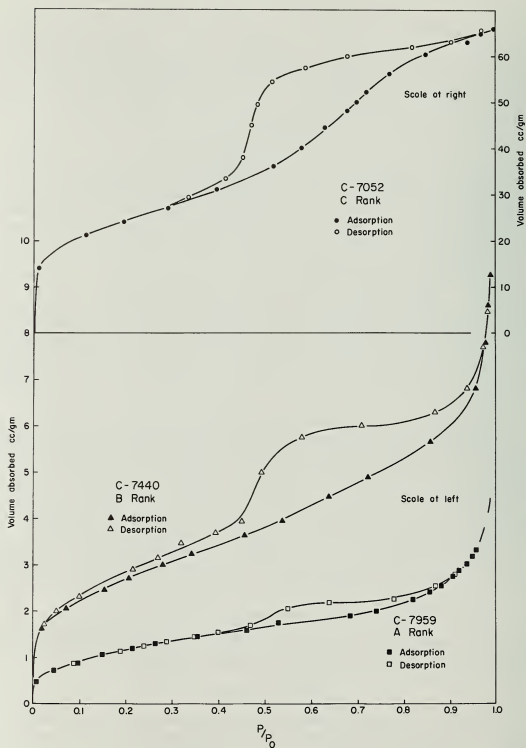
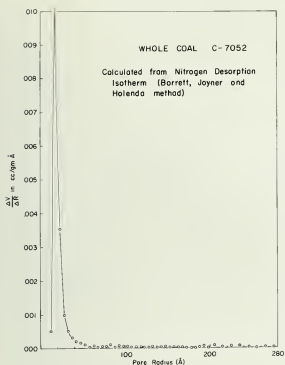Fig. 1 - Nitrogen isotherms for coals of A, B, and C rank.

Fig. 2 - Pore volume distribution curve

different from that used for nitrogen. For one thing, the total pressure range involved is from zero to 30 millimeters of mercury, which necessitates the use of more refined techniques of measurement in order to get reliable data. For another, varying ambient temperature in the laboratory makes it difficult, if not impossible, to obtain accurate pressure-volume measurements of the total amounts of water taken up by the sample. However, if weight methods are used, good data can be obtained.

Figure 3 presents water adsorption and desorption isotherms for high-volatile A, B, and C bituminous coals. It will be observed that the desorption isotherm with water does not rejoin the adsorption branch until the pressure reaches a value of zero, whereas in the case of the nitrogen isotherms the adsorption and desorption are superposed, or nearly so, at low values of P/P_0.

Figure 4 presents water adsorption isotherms for banded ingredients of a high-volatile C bituminous coal (C-7052). The h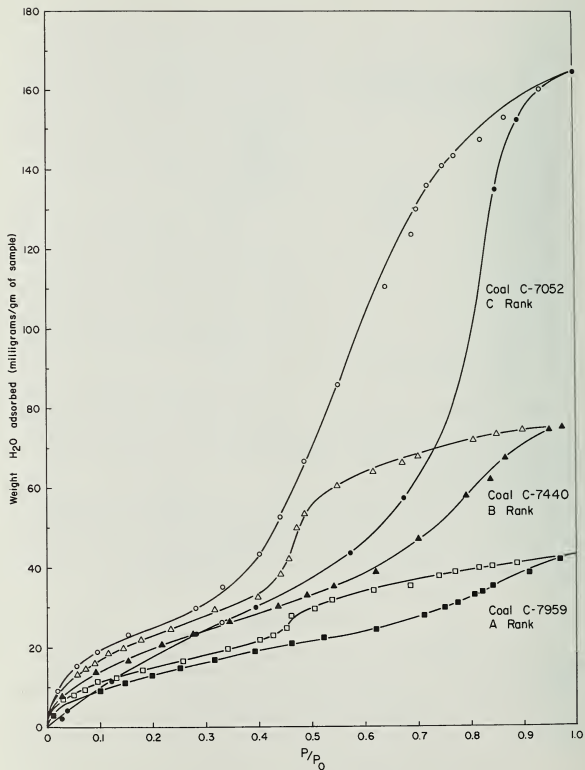ysteresis loops, as might be expected, are of largest area for the vitrain, of intermediate area for the clarain, and of smallest area for the fusain. The isotherm for the whole coal is plotted on the same figure for comparison.

There are at least two obvious reasons for this difference in behavior between nitrogen and water at the lower pressures. First, the nitrogen isotherms are measured at a temperature very near the boiling point of liquid nitrogen, while the water isotherms are measured at room temperature. Second, the size of the water molecule is considerable less than that of the nitrogen molecule. It is probable that the first reason is much more important then the second.

CONCLUSIONS

Illinois high-volatile C bituminous coals are much more porous than the Illinois high-volatile A and B bituminous coals and, consequently, have much greater specific surface. The high-volatile B bituminous coals have greater specific surfaces than do the Illinois high-volatile A bituminous coals.

The pore size distribution computations indicate that for all coals entering into this study, there is a high peak in the region of 40 Å diameter. The position of this peak does not appear to vary much with coal rank.

An interesting feature of the surface area studies is that the surface areas of the small number of anthracites studied were considerably greater than those of the high-volatile A and the low-volatile bituminous coals studied.
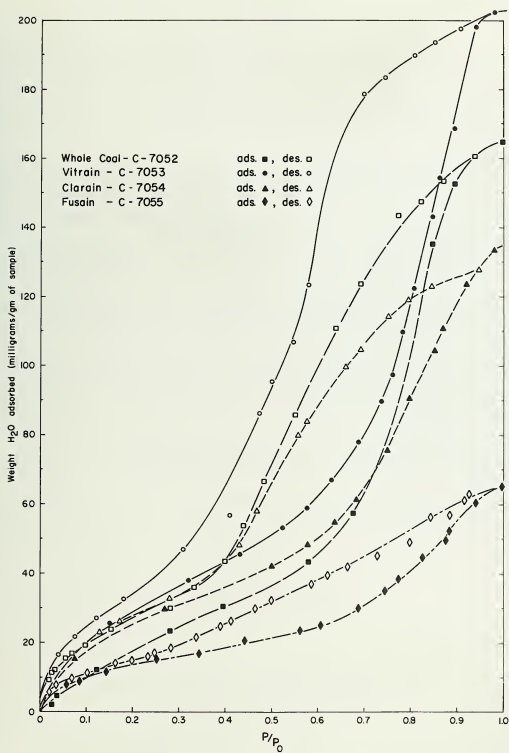
Fig. 3 - Water isotherms whole coals.

Fig. 4 - Water isotherms, banded ingredients.

REFERENCES

Barr, W. E., and Anhorn, Victor J., 1949, Scientific and industrial glass blowing and laboratory techniques: Pittsburgh, Instruments Publishing Co., p. 277.

Barrett, Elliott P., Joyner, Leslie G., and Halenda, Paul P., 1951, The determination of pore volume and area distribution in porous substances. I. Computations from nitrogen isotherms: Am. Chem. Soc. Jour., v. 73, p. 373-380.

British Coal Utilisation Research Association, 1944, Proceedings of a conference on the ultra-fine structure of coals and cokes, The Royal Institution, London, June, 1943: London, British Coal Utilisation Research Assoc., 366 p.

Brunauer, Stephen, 1945, The adsorption of gases and vapors. Volume I, Physical adsorption: Princeton, Princeton University Press.

Brunauer, Stephen, Emmett, P. H., and Teller, Edward, 1938, Adsorption of gases in multimolecular layers: Am. Chem. Soc. Jour., v. 60, p. 309-319.

Emmett, P. H., and Brunauer, Stephen, 1937, The use of low temperature van der Waals adsorption isotherms in determining the surface area of iron synthetic ammonia catalysts: Am. Chem. Soc. Jour., v. 59, p. 1553-1564.

Harkins, W. D., and Jura, George, 1944, Surfaces of solids. XIII. A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surface of a solid: Am. Chem. Soc. Jour., v. 66, p. 1366-1373.

Holmes, James, and Emmett, P. H., 1947, Alteration of the size and distribution of pores in charcoals: Jour. Physics and Colloid Chem., v. 51, p. 1276-1307.

Maggs, F. A. P., 1952, Anomalous adsorption of nitrogen at 90°K: Nature, v. 169, no. 4306, p. 793-794.